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(21) International Application Number: PCT/BE98/00153 (22) International Filing Date: 15 October 1998 (15.10.98) (30) Priority Data: 97870163.9 22 October 1997 (22.10.97) EP (71) Applicant (for all designated States except US): N.V. BEKAERT S.A. [BE/BE]; Bekaertstraat 2, B-8550 Zwevegem (BE). (72) Inventors; and (75) Inventors/Applicants (for US only): DECLERCQ, Dries [BE/BE]; Menenstraat 132, B-8560 Wevelgem (BE). VANBRABANT, Johan [BE/BE]; Deerlijkstraat 221, B-8550 Zwevegem (BE). MAUER, Daniel [BE/BE]; Allée des Peupliers 21, B-7320 Bernissart (BE). GARNIER, Francis [FR/FR]; 17, Villa Remy, F-94500 Champigny (FR). NOGUES, Claude [FR/FR]; 31, rue de Lagny, F-94300 Vincennes (FR). LANG, Philippe [FR/FR]; 76, rue de la Jarry, F-94300 Vincennes (FR). MICHALITSCH, Richard [AT/AT]; A-2305 Kopfstetten 72 (AT). (74) Agents: VANDEBERG, Marie-Paule et al.; Office Kirkpatrick S.A., Avenue Wolfers 32, B-1310 La Hulpe (BE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: MEANS AND METHODS FOR ENHANCING INTERFACIAL ADHESION BETWEEN A METAL SURFACE AND A NON-METALLIC MEDIUM AND PRODUCTS OBTAINED THEREBY (57) Abstract For enhancing the interfacial adhesion between a metal surface and a non-metallic medium there are provided methods and means whereby use is made of a bifunctional coupling agent having a first terminal function for adhering to the metal surface and having a second terminal function for adhering to the non-metallic medium. The two functional groups of the coupling agent are spaced apart by a spacing group. Metal elements coated with said bifunctional coupling agent and such coated metal elements which are covered with a non-metallic medium. Use of such coated elements as reinforcement elements.		

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MEANS AND METHODS FOR ENHANCING INTERFACIAL ADHESION
BETWEEN A METAL SURFACE AND A NON-METALLIC MEDIUM AND
PRODUCTS OBTAINED THEREBY.

5 The present invention concerns a method for improving the interfacial adhesion between a metal and a non-metallic medium, an interfacial adhesion promoter for use in said method and metal objects presenting improved interfacial adherence to non-metallic media.

10 Metal surfaces are often provided with organic coatings such as paints, varnishes and lacquers with a view to protecting the metal surfaces against mechanical damage or corrosion and/or to improve their appearance. An alternative is to coat a metal surface with a plastic or
15 rubber coating.

 Metal elements, such as wires, are also embedded in organic, e.g. rubber, or inorganic, e.g. cement or concrete, material for the reinforcement of the latter.

 In all the above cases a good adherence between
20 the metal surface and the surrounding medium is of major importance for the desired effect to be achieved.

 Several methods have been developed to improve the interfacial adhesion between a metal and a non-metallic medium. Typically, a primer coating is applied directly
25 onto the metal surface, whereby said primer has an affinity both for the metal surface and for the non-metallic medium which is higher than the interfacial affinity between the metal and the non-metallic medium. The non-metallic medium is subsequently applied onto the coated metal surface.

30 To be effective, the primer should cover the metal surface entirely, leaving no part of it exposed. Said primer coating preferably also possesses corrosion inhibiting properties.

 Efforts to develop new primers or to improve
35 existing primers have generally been directed towards a

specific field of application, i.e. either metal-paint systems, or metal-plastic systems or else metal-inorganic material systems.

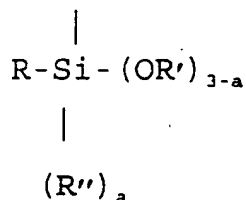
An example of a primer for metal-paint systems is known from US patent 5,326,594. Said known primer is obtained by first rinsing the metal surface with an alkaline silicate and aluminate solution and drying same to obtain an inorganically coated surface, whereafter the thus coated surface is rinsed with an aqueous solution of a hydrolyzed silane and a hydrolyzed cross linking agent. After drying a silane film is formed. The first, inorganic layer is said to confer onto the silane film an oriented molecular structure which is believed to improve the adhesion between the silane film and the paint to be applied thereto.

An example of a primer for metal-cement systems is known from international patent application WO 96/32522. The method therein disclosed comprises the phosphatization of the metal surface in a Fe-, Ca/Zn-, Zn- or Mn-phosphate bath, followed by a surface treatment with an aqueous solution of pacifying compounds such as nitrites, chromates, hydrazine or hydrazine derivatives and hydroxylamines or hydroxylamine derivatives, and/or organic corrosion inhibitors.

A further example of a primer for metal-cement systems is known from US 2,992,131. As disclosed therein, the metal surface is initially freed of any scale and oxide, followed by depositing an insoluble amorphous or crystalline heavy metal phosphate coating on said surface, whereafter the surface is coated with a coating composition comprising an organic film forming medium, the composition of the coating being thus that it is chemically resistant to cement or concrete while simultaneously presenting high bond strength to both the cement or concrete and to the metal surface.

Inter alia due to the known corrosion inhibiting effect of phosphatization, the above-described metal-cement primer also provides corrosion protection to the metal surface.

5 A method for improving surface adhesion in a metal-rubber system is known from EP-A-738 748. According to said method a stainless steel surface, containing specific quantities of carbon, nickel and chromium and containing a minimum amount of martensite and a maximum
10 amount of austenite, is first modified by means of an activation process whereby the metal surface is for example treated with an acid solution or by plasma treatment. The thus activated metal surface is then treated with a silane film. The preferred silane for use in this method is a
15 bifunctional silane of the formula



20 whereby $0 \leq a \leq 2$, R is an organic radical having at least one function reactive towards at least one element of the rubber composition, $\text{OR}_=$ is a group reactive towards oxides or hydroxides present on the activated metal surface, whereas R'' may be hydrogen, a cyclic or acyclic organic
25 radical or a halogen radical.

The present invention aims to improve the adhesion between a metal surface and a range of non-metallic media.

30 The present invention can advantageously be used in the field of elastomer or cement reinforcement.

The present invention is more particularly useful for the reinforcement of elastomers and concrete, in particular high performance concrete by means of metal elements such as elongated steel elements.

Elongated steel elements for the reinforcement of elastomers such as tyres (rubber), conveyor belts (rubber), hoses (rubber) or timing belts (polyurethane or rubber) typically have the following features. As to their form, they are present as single steel filaments or steel wire, as twisted steel cord or as woven steel cord. The diameter of the individual steel filaments or steel wires range from 0.04 mm for the reinforcement of timing belts, to 2.0 mm for the reinforcement of the bead area of tyres.

The steel composition generally is along the following lines : a carbon content between 0.60 % by weight and 1.10 % by weight, a manganese content between 0.40 % by weight and 0.70 % by weight, a silicon content between 0.10 % by weight and 0.40 % by weight, a maximum sulfur content of 0.05 % by weight, a maximum phosphorus content of 0.05 % by weight. Micro-alloying with particular elements such as chromium, nickel, vanadium, boron, cobalt, copper, molybdenum, etc. is not excluded for amounts ranging from 0.01 % by weight to 0.80 % by weight.

The steel wires or steel filaments are conveniently coated with a metallic layer such as brass (63.5-67.5 % by weight Cu + 36.5-32.5 % by weight Zn), bronze (Cu + Zn + max 3 % by weight Sn), zinc or a zinc alloy (example: Zn + 2 à 12 % by weight Al + misch metal, a tin-zinc alloy or a zinc-cobalt alloy) in order to facilitate the final drawing steps and/or to provide an adhesion with the elastomer or to provide a corrosion resistance.

The tensile strength of the steel wires or steel filaments ranges from 1500 MPa (1 MPa = 1 N/mm²) to 4000 Mpa and more and is mainly dependent upon the final diameter, the exact composition (amount of carbon + amount of micro-alloying components) and on the amount of final drawing.

Elongated steel elements for the reinforcement of concrete have the form of steel fibres. Such steel

fibres typically have a length ranging from 3 mm to 60 mm, a thickness ranging from 0.08 mm to 1.20 mm and a tensile strength greater than 1000 MPa, e.g. greater than 1500 MPa, or greater than 2000 MPa. The steel fibre is conveniently
5 provided with anchorages for mechanically anchoring the fibre in the concrete. The length-to-thickness ratio ranges between 50 and 200. The concentration of the fibres in concrete may range from 25 kg/m³ to 80 kg/m³.

The term "thickness" of a steel fibre refers to
10 the smallest cross-sectional dimension of a straight steel fibre without the anchorages.

The term "anchorage" refers to any deviation from a straight steel fibre with a uniform transversal cross section where the deviation helps to improve the anchorage
15 or staying of the steel fibre in the concrete.

For the reinforcement of high-performance concrete or mortar, the steel fibres have the same steel composition as for the reinforcement of elastomers. For the reinforcement of normal or conventional concrete (i.e.
20 concrete with a compression strength lower than 60 MPa), the the carbon content is lower than 0.60 % by weight since the tensile strength of the fibres is not so critical.

The steel fibres may or may not be provided with a metallic coating such as brass or zinc. Here, the reason
25 for the metallic coating is not to create an improved adhesion with the concrete but rather to facilitate the final drawing steps or to provide a corrosion resistance.

The terms "high-performance" "concrete" or "mortar" refer to concrete or mortar, the compression
30 strength of which is higher than 75 MPa, e.g. higher than 200 MPa. The compression strength is the strength as measured by ASTM-Standard N° C39-80 on a cube of concrete of 150 mm edge, whereby the cube is pressed between two parallel surfaces until rupture.

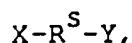
In comparison with conventional concretes, high-performance concretes are characterized by :

- (a) a relatively low water/cement ratio (smaller than 0.45);
- 5 (b) the addition of superplasticizers which much increase the workability of concrete in spite of the low water/cement ratio;
- (c) the addition of mineral additives such as silica fumes, fly ashes, blast furnace slag, pulverized fuel, micro-
- 10 fillers and/or pozzolans and/or the addition of chemical additives such as water glass and tensides.

Next to the reinforcement by steel fibres, concrete and, more in particular, high performance concrete may also be reinforced by steel cables which may be

15 prestressed.

According to the present invention there is provided a bifunctional coupling agent of the formula



whereby functional group X enables a strong adhesion of the

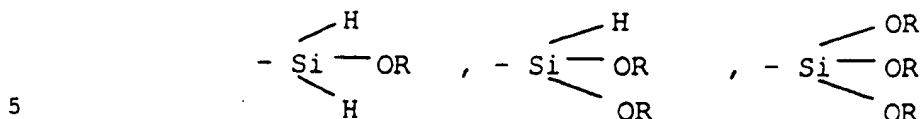
20 coupling agent to the metal surface, functional group Y provides for strong adhesion to the non-metallic medium and R^S acts as a spacing agent between functions X and Y.

The present invention concerns a primer composition for increasing the surface adhesion between a

25 metal surface and a non-metallic medium. Said primer composition comprises a practical amount of a bifunctional coupling agent of formula $X-R^S-Y$. By a practical amount of $X-R^S-Y$ is meant, a concentration of said compound in the primer composition sufficient to produce a monolayer of

30 $X-R^S-Y$ on the metal surface, given the primer application method used.

The constituent part X may be a



whereby each -OR is the same and is a methoxy or an ethoxy group.

X may also be a mono-, di- or tri-chlorosilane group or a mono-, di- or tri-bromosilane group.

Alternatively, X may be an acid function selected from the group comprising $-\text{CO}_2\text{H}$, $-\text{PO}_3\text{H}_2$, and $-\text{SO}_2\text{H}$, their acid anhydride and their acid chloride group.

X can also be an organometallic compound of the formula $-\text{M}(\text{OR})_n$, whereby M is a metal atom selected from the group comprising Al, Sn, B, Ti and V, and whereby each -OR is the same and is a methoxy or an ethoxy group, n being the ligand number corresponding to the metal M.

Optionally X can also be $-\text{MCl}_n$, whereby M and n are as defined hereinabove.

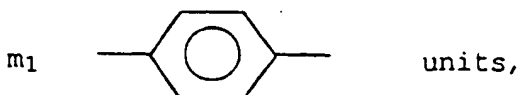
X can furthermore be a phthalocyanin or a phthalonitril group.

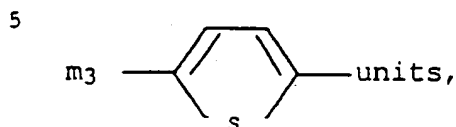
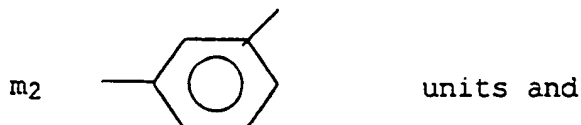
X can also be a monothiol or a monothiolate group.

Constituent part R^{S} may be a $-(\text{CH}_2)_n-$ chain, whereby $2 \leq n \leq 20$ and whereby said chain may be unsubstituted, partially halogenated or perhalogenated.

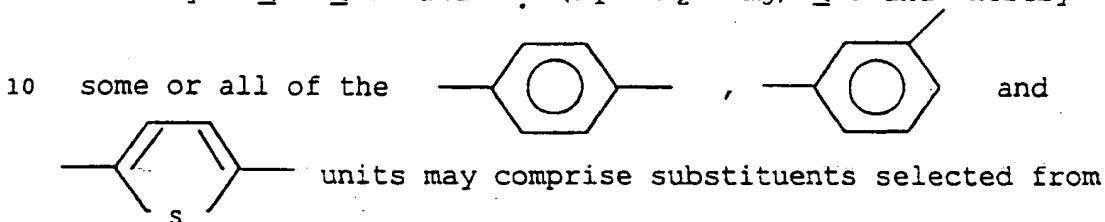
Alternatively R^{S} may be a continuous chain consisting of:

n partially halogenated or perhalogenated $-(\text{CH}_2)-$ units,



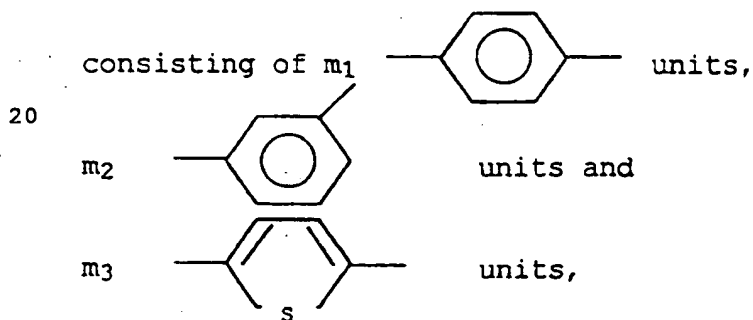


whereby $2 \leq n \leq 20$ and $0 \leq (m_1 + m_2 + m_3) \leq 3$ and whereby



the group comprising: $-(CH_2)_iCH_3$ with $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$ with $0 \leq j \leq 4$, $-O(CF_2)_jCH_3$ with $0 \leq j \leq 4$, $-C \equiv N$ and $-NH_2$.

Constituent part R^S may further be a chain



25 whereby $2 < m_1 + m_2 + m_3 < 6$, and whereby said units may comprise substituents selected from the group comprising : $-(CH_2)_iCH_3$ with $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$ with $0 \leq j \leq 4$, $-O(CF_2)_jCH_3$ with $0 \leq j \leq 4$, $-C \equiv N$ and $-NH_2$.

Constituent part Y may be an unsaturated terminal carbon-carbon double or triple bond.

Y can also be an acrylic or methacrylic acid

group and its methyl or ethyl esters.

Y may be of the form -NH_2 or -NHR , whereby R is a methyl or ethyl group.

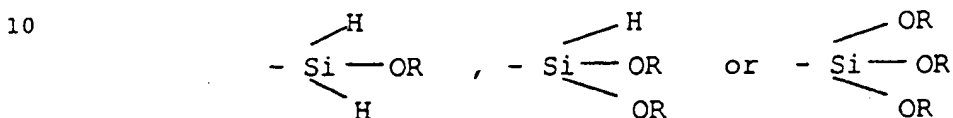
Y can also be $\text{-C}\equiv\text{N}$.

5 Y can further be an activated carboxylic ester group.

Alternatively, Y can be an aldehyde group.

Y can be an epoxide group.

Optionally, Y can be any one of the following:



whereby each OR is the same and is a methoxy or an ethoxy group. Alternatively Y can be a mono-, a di- or a tri-chlorosilane group or a mono-, di- or tri-bromosilane group. When Y is an alkoxysilane group, a chloro- or bromosilane group, R^{S} must be a $\text{-(CH}_2\text{)}_3\text{-}$ or a $\text{-(CH}_2\text{)}_4\text{-}$ chain which may be unsubstituted, partially halogenated or perhalogenated.

20

As a further alternative Y may be a functional group capable of forming a complex with at least one ingredient of the non-metallic medium concerned. This ingredient may be present in the non-metallic medium as such, for example as a pigment, or may have been added to the non-metallic medium specifically so as to allow the formation of a complex with constituent part Y.

25

As yet a further alternative Y may be -Si-OH or -Si-ONa .

30 In the context of the present invention, it is to be noted that, even though chloride-containing constituent parts X such as -MCl_n and -SiCl_3 may provide high quality adhesion to the metal surface, the use of chloride containing constituent parts X, R^{S} and Y is contra-

indicated if the metal surface is liable to corrode in the presence of chloride ions. This is specifically the case with steel or iron-containing metal surfaces.

When X is an alkoxysilane, X is preferably a trimethoxysilane or a triethoxysilane group.

If X is a monothiolate group, it is preferably -SNa or -SK.

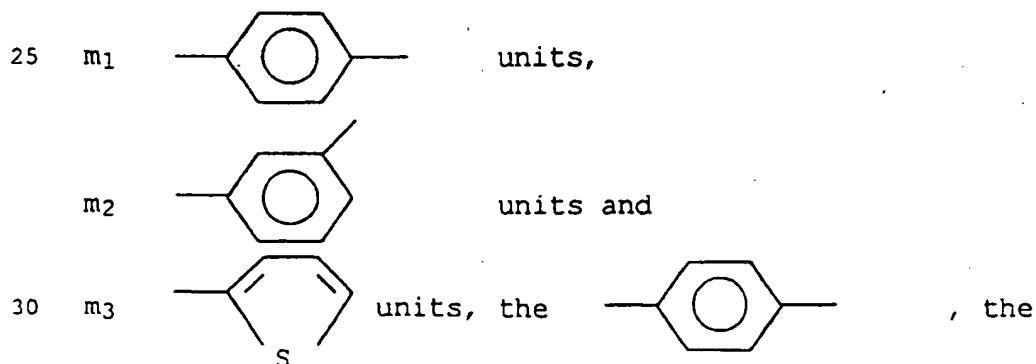
When R^S is an unsubstituted, partially halogenated or perhalogenated $-(CH_2)_n-$ chain, optionally $2 < n < 16$ or $2 < n < 10$.

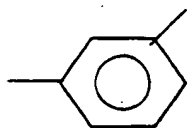
In this case, n is preferably equal to or greater than 4 and most preferably situated between 6 and 12, the values 6 and 12 being included.

Alternatively when R^S is an unsubstituted, partially halogenated or perhalogenated $-(CH_2)_n-$ chain, $n > 12$.

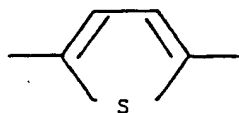
When R^S is a partially halogenated or perhalogenated $-(CH_2)_n-$ chain, the halogenation is preferably a fluorination. A perfluorinated $-(CH_2)_n-$ chain is most preferred.

According to the embodiment of the present invention whereby R^S is a continuous chain consisting of: n partially halogenated or perhalogenated $-(CH_2)-$ units,





and/or



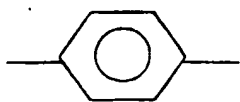
units

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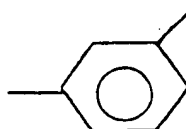
may be adjacent constituent part X, adjacent constituent part Y or may be attached to constituent part X and/or to constituent part Y via one or more of the $-(CH_2)-$ units.

10

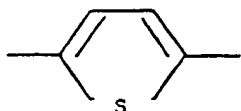
Said



,



and/or



units may be grouped together or

15

interspersed with one or more $-(CH_2)-$ units.

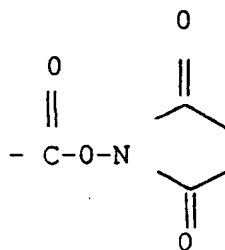
If constituent part Y is a terminal double carbon-carbon bond then R^S can advantageously be such that $-R^S-Y$ terminates in any one of the following groups: vinyl, allyl, styryl, thienylvinylene, phenyl or pyrrole groups.

20

If Y is an alkoxysilane, Y is preferably a trimethoxysilane or triethoxysilane group.

According to an advantageous embodiment of the invention, Y is an activated carboxylic ester group of the formula

25



30

When Y is a complex forming group, it can advantageously be chosen among :

HO_2CCO_2H , $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, $[-CH_2O(CH_2CH_2O)_nCH_3$

whereby

$3 \leq n \leq 6$], and crown and aza crown ethers consisting of

4,5 or 6 $-\text{OCH}_2\text{CH}_2-$ units.

The present invention equally concerns a metal element having at least part of its metal surface covered with an organic monolayer obtained by reaction of a bifunctional coupling agent of the formula $\text{X-R}^{\text{S}}-\text{Y}$ on the metal surface, whereby $\text{X-R}^{\text{S}}-\text{Y}$ is as described hereinabove. Such a metal element presents advantageous surface adhesion properties with regard to one or more of a range of non-metallic media.

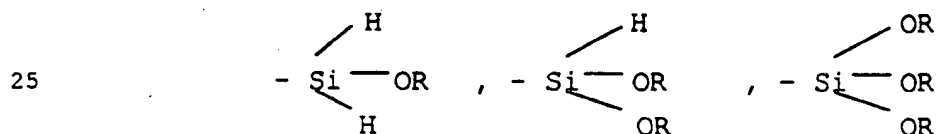
The metal surface of the metal element according to the invention may mainly be made of Al, Fe, Ni, Cu, Zn, Ag or alloys of these metals.

The metal element according to the invention may consist of a basic metal element which is coated with a metal coating of a brass, bronze, zinc or zinc alloy and whereby the said metal surface is formed by said coating.

In the case of a metal-coated basic metal element, the basic metal element may be made out of steel.

If the metal surface of the metal element according to the invention is mainly made of Zn, the constituent part X may advantageously be one of the following:

a)



whereby each $-\text{OR}$ is the same and is a methoxy or an ethoxy group,

b) mono-, di- and tri-chlorosilane groups or mono-, di- or tri-bromosilane groups,

c) $-\text{CO}_2\text{H}$, $-\text{PO}_3\text{H}_2$, $-\text{SO}_2\text{H}$, their anhydride and acid chloride group,

d) a monothiol or a monothiolate group, or

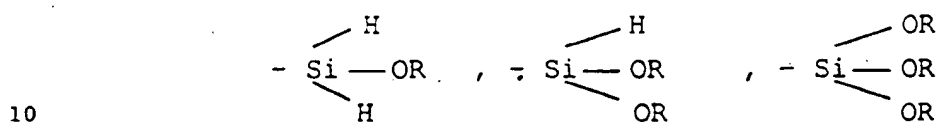
e) a phthalocyanin or a phthalonitril group.

When the metal surface is mainly made of a Zn-Al alloy, the constituent part X is preferably :

a) $-M[OR]_n$, whereby M is Al, Ti, V, B or Sn and whereby each

5 $-OR$ is the same and is a methoxy or an ethoxy group,

b)



whereby each $-OR$ is the same and is a methoxy or an ethoxy group,

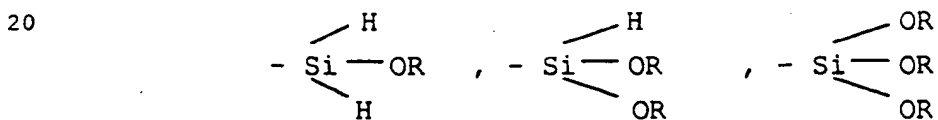
c) a chloro- or bromosilane group,

d) $-\text{CO}_2\text{H}$, $-\text{PO}_3\text{H}_2$, or $-\text{SO}_2\text{H}$.

15 When the metal surface is mainly made of a Zn-Cu alloy, the constituent part X is preferably :

a) a phthalocyanin or a phthalonitril group,

b)

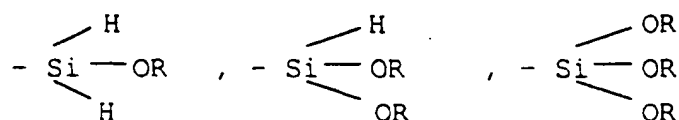


whereby each $-OR$ is the same and is a methoxy or an ethoxy group,

25 c) mono-, di- and tri-chlorosilane groups or mono-, di- or tri-bromosilane groups.

When the metal surface is mainly made of a Sn-Zn alloy, constituent part X is preferably one of the following :

30 a)



whereby each -OR is the same and is a methoxy or an ethoxy group,

b) mono-, di- and tri-chlorosilane groups and mono-, di-
5 and tri-chlorosilane groups,

c) $-CO_2H$, $-PO_3H_2$, and $-SO_2H$, and their acid anhydride and acid chloride groups.

Of the latter three acid groups, $-PO_3H_2$ is preferred.

10 When the metal surface is mainly made of a steel, constituent part X is advantageously one of the following :

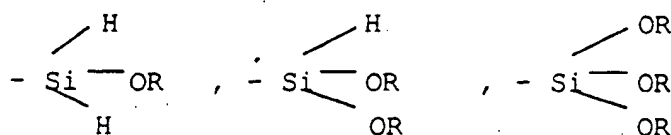
a) a monothiol or a monothiolate group,
15 b) a phthalocyanin or a phthalonitril group.

As stated above, constituent part Y may be $-NH_2$ or $-NHR$, whereby $-R$ is a methyl or an ethyl group. This embodiment of the present invention is particularly indicated when the part of the metal surface which is
20 covered with the monolayer is further covered with a polyurethane coating. When the metal element is an elongated metal element and the constituent part Y of $X-R^S-Y$ is $-NH_2$ or $-NHR$, such an elongated element can advantageously be used
25 for the reinforcement of polyurethane.

When constituent part Y is a double or triple carbon-carbon bond, including those embodiments whereby $-R^S-Y$ terminates in a vinyl, an allyl, a styryl, a thienylvinylene, a phenyl or a pyrrole group, the part of
30 the metal surface which is covered with the monolayer is advantageously further covered with a polyethylene, polypropylene, polybutadiene, a copolymer of at least two of ethylene, propylene and butadiene, or a rubber coating. When constituent part Y is of this type, elongated metal

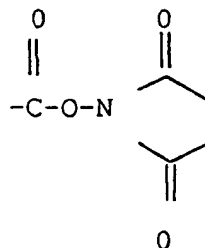
elements according to the invention coated with such an X-R^S-Y monolayer can advantageously be used for the reinforcement of polyethylene, polypropylene, polybutadiene, a copolymer of at least two of ethylene, propylene and butadiene, and rubber.

When constituent part Y is a



whereby each -OR group is the same and is a methoxy or an ethoxy group, or, if the metal surface so allows, a mono-, di- or tri-chlorosilane group or a mono-, di- or tri-bromosilane group, and whereby R^S is a straight -(CH₂)₃- or -(CH₂)₄- alkyl chain, which may be unsubstituted, partially halogenated or perhalogenated, the part of the metal surface which is covered with the monolayer is advantageously further covered with a siloxane coating. As already mentioned above, fluorinated, and particularly perfluorinated alkyl chains are preferred.

If constituent part Y is an activated ester group, and in particular when Y is



30 the part of the metal surface which is covered with the monolayer is advantageously further covered with a polyacrylate coating. In the case of such a constituent part Y, an elongated metal element according to the invention, the surface of which is covered with a monolayer

of $X-R^S-Y$ can advantageously be used for the reinforcement of a polyacrylate.

When Y is an epoxide group, an aldehyde group, a terminal double or triple carbon-carbon bond, the part of the metal surface which is covered with the monolayer is advantageously further covered with a polyamide coating. Elongated metal elements coated with a $X-R^S-Y$ monolayer of this type can advantageously be used for the reinforcement of polyamide.

When constituent part Y is an ion complexing group capable of forming a complex with an ingredient of concrete, in particular when Y is HO_2CCO_2H , $(HO_2CCH_2)NCH_2CH_2N(CH_2CO_2H)_2$ $[-CH_2O(CH_2CH_2O)_nCH_3$ whereby $3 \leq n \leq 6]$ or a crown ether or an aza crown ether consisting of 4,5 or 6 $-OCH_2CH_2-$ units, the use of elongated metal elements the surface of which is covered with a monolayer of $X-R^S-Y$ for the reinforcement of concrete is particularly indicated.

Complexing constituent parts Y may also be used when the metal element is to be coated with or incorporated in a non-metallic medium comprising a sufficiently high concentration of ingredients, such as pigments, with which the complexing group Y can form a stable complex.

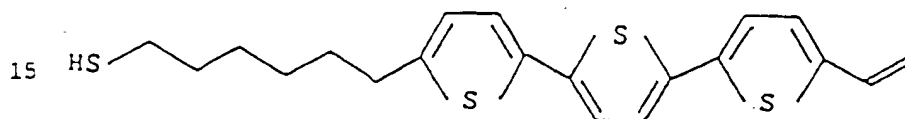
Bifunctional coupling agents of the present invention present the important tendency of forming Self-Assembled Monolayers on the metal surface, i.e. when applied onto the metal surface, then the molecules automatically tend to form a structured, packed monolayer whereby the constituent parts X are attached to the metal surface and whereby the substituent parts Y point away from the metal surface. This property of the bifunctional coupling agents $X-R^S-Y$ provides an important contribution to the effectiveness of the coupling agent and allows for an easy realisation of the monolayer onto the metal surface.

Methods for preparing molecules corresponding to the bifunctional coupling agents according to the present invention are known from the state of the art. Many are moreover commercially available.

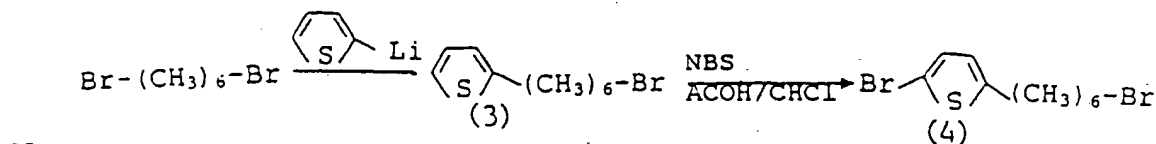
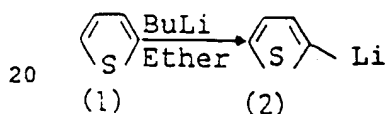
By way of example, a preparation method is described hereinbelow for three of the bifunctional coupling agents according to the present invention.

EXAMPLE 1: Preparation method for 6-(5"-vinyl-2,2':5',2"-terthiophene-5yl)hexanethiol

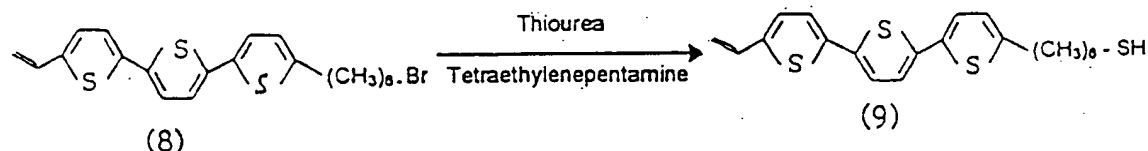
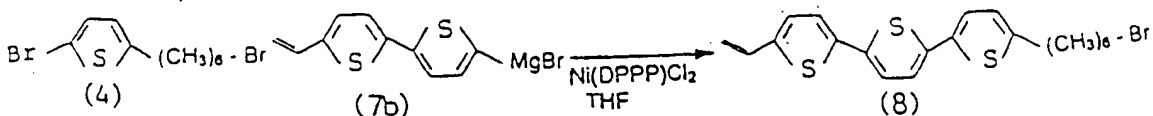
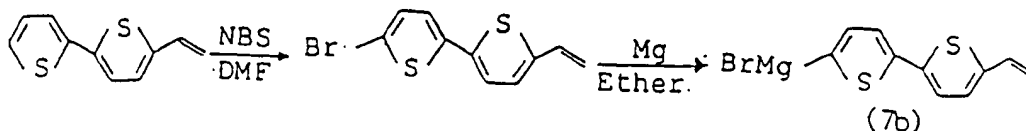
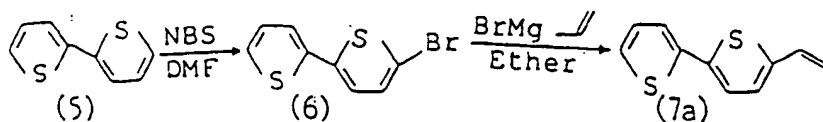
6-(5"-vinyl-2,2':5',2"-terthiophene-5yl)hexanethiol :



Reaction steps:



Parallel procedure:



6-(2-thienyl)-bromohexane (compound 3) :

60 ml of anhydrous ether and 0.1 mole (8.4 g) of thiophene

(compound 1) were cooled to -80°C under inert atmosphere,

66 ml (0.11 mol) n-BuLi solution (2.5 M in hexane) were slowly added through a dropping funnel. The reaction

mixture was stirred for about one hour, which led to a nearly quantitative yield of 2-lithiothiophene

(compound 2). Compound 2 then was transferred under inert conditions to another dropping funnel and added to

1,6-dibromohexane in anhydrous ether. Raising the temperature up to room temperature effected a connection of

the alkyl branch to the aromatic system,

6-(2-thienyl)bromohexane (compound 3). The reaction mixture was hydrolysed with 1N HCl and neutralized with NaHCO_3 .

Extractive workup with ether gave 58 % yield of 6-(2-thienyl)bromohexane. The product can be purified by

distillation under reduced pressure. (b.p. (1 mm Hg) = 78°C).

6-(5-bromothiophen-2-yl)bromohexane (compound 4)

0.005 Mole (12.25 g) of 2-(6-bromohexyl)thiophene (compound 3) were solubilized in 80 ml of the solvent. 0.055 mole n-bromosuccinimide (NBS, 9.78 g) were added in small quantities under continuous stirring and ambient
5 conditions. Chromatographic control showed that the reaction was finished after one hour. The product was extracted with several portions of ether. The etherous solution was washed with NaHCO_3 , dried with MgSO_4 and the ether evaporated. The liquid product was purified using
10 column chromatography over silica (70-200 mesh). Elution with hexane gave 14.9 g (92 %) 6-(5-bromothien-2-yl) bromohexane (compound 4).

6-(5''-vinyl-2,2':5'2"-terthien-5-yl)bromohexane
15 (compound 8)
0,05 mole (9.97 g) of 2,2-bithiophene (5) were solubilized in 40 ml DMR, cooled to -40°C and 0.055 mole (10.7 g) NBS were slowly added. Stirring for 12 hours and workup as described resulted in the formation of 10.2 g (83 %)
20 5-bromo-2,2'bithiophene (6). 6.1 g of compound 6 (0.0025 mole) in 30 ml of anhydrous ether were added dropwise under inert atmosphere to 2.7 g of vinyl-magnesiumbromide (0.025 mole) in 30 ml of ether. The reaction mixture was refluxed for 5h resulting in a
25 Grignard coupling reaction. The mixture was hydrolyzed with 5 % HCl_{aq} and worked up by evaporation of the solvent. The product was used without further purification. In the following step the bromination procedure was repeated on the other terminal α -position using once more NBS in
30 dimethylformamide and resulting in the formation 5-vinyl,5'bromo--2,2'-biothiophene, which was subsequently converted to the corresponding Grignard compound by adding 0.02 mole (3.8 g) of the brominated product to 0.5 g magnesium turnings in 100 ml ether. The reaction solution
35 was gently refluxed for 2 hours and subsequently

transferred to another experimental set. The Grignard solution was slowly dropped into a mixture of 8.15g (0.025 mole) of compound (4) with (1 mole %) NiDPPPCl₂ (1,3-bis(diphenylphosphino)-propanedichloronickel (II) in 5 40 ml anhydrous THF (tetrahydrofuran). Refluxing overnight resulted in a Grignard cross coupling reaction to 6(5''-vinyl-2,2':5'2''-terthien-5-yl)bromohexane (8): The workup consisted of hydrolyzing with several ml of 1N HCl, extraction with small portions of ether, drying the solvent 10 with MgSO₄(sicc.)and evaporation of the solvents. The product (8) was purified by a silica column chromatography (70-200 mesh). Yield : 7.7 g of 6-(5''-vinyl-2,2':5'2''-terthien-5-yl)bromohexane (64 %)

15

6-(5''-vinyl-2,2':5'2''-terthien-5-yl)hexanethiol
(compound 9)

A mixture of 3 ml of ethyleneglycol and 0.83 g (0,011 mole = 1.1 eq) of thiourea was stirred at 80°C under 20 inert atmosphere until the solution became homogeneous 4.4 g of compound (8) were added in one portion and the reaction temperature was raised to 130° to 140°C. These conditions were kept for about 2 hours to form the isothioronium salt (homogeneous solution), which finally was 25 cleaved by the addition of 0.9 g (0.5 eq) of tetraethylenepentamine.

After additional 3 hours the mixture was worked up. The reaction solution was diluted with ether and 1N HCl. The following extraction procedure also was carried out under 30 inert atmosphere as far as possible to avoid oxidative coupling of the thiol functions to disulfides. The gathered organic fractions were washed to neutral and dried with MgSO₄. The solvent was evaporated and the product recrystallized from hexane. 2.4 g (61 %) of 6-(5''-vinyl-

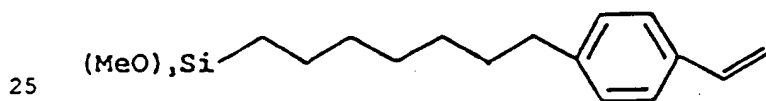
2,2':5'2"-terthien-5-yl)hexanethiol (compound 9) were isolated. The overall yield of the 6-step synthesis was 23 %.

The described synthesis shows that the type of bifunctional molecule according to the present invention is synthetically accessible and available in reasonable quantities. Nevertheless in industrial production processes time plays an important role influencing directly the costs of fabrication. Thus, in practice it may be advisable to keep the complexity of the molecule chosen as coupling agent as low as possible. It may be preferable to avoid constructing too long alkyl and aromatic chains.

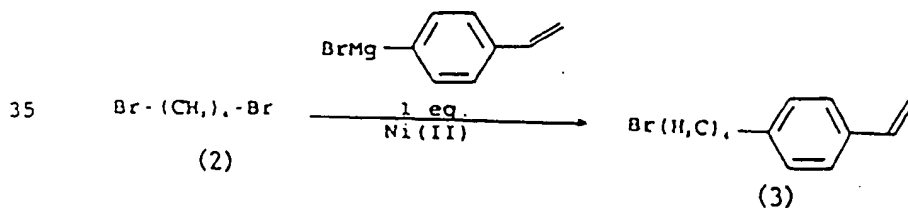
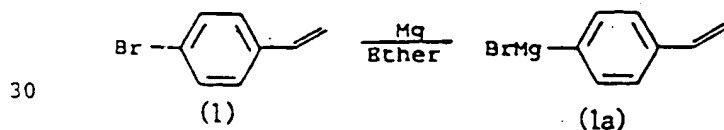
Hereinbelow are described synthesis-paths which are simpler from a practical point of view and allow for any production of large quantities of the molecules. Furthermore, important precursors are available commercially.

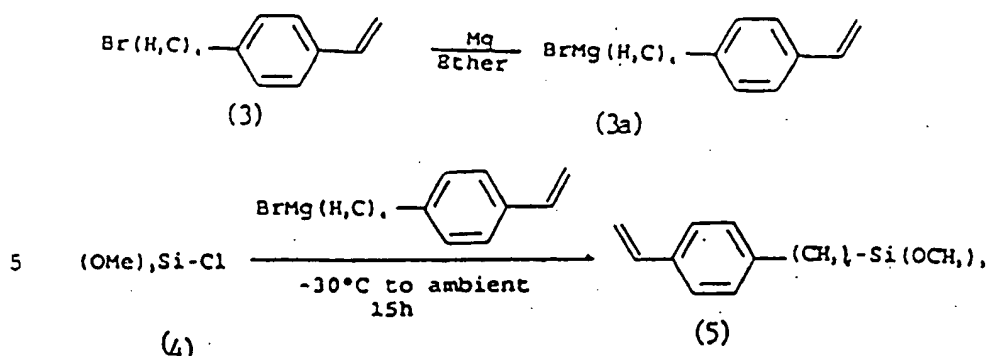
EXAMPLE 2: Preparation method for 6-(p-styryl)hexyl-trimethoxysilane

6-(p-styryl)hexyl-trimethoxysilane :



Reaction steps :





1-bromo-6(p-styryl)-hexane compound (3) :

0.1 mole (18.3 g) p-styrenebromide (1) were added dropwise
 10 to 2.4 g magnesium turnings in 200 ml of anhydrous ether,
 the mixture was agitated for 2 hours under argon atmosphere
 und slight cooling. Subsequently the solution of the
 formed Grignard compound was transferred to another
 experimental set, where it was added slowly to
 15 3 equivalents (73.1 g) 1,6-dibromohexane in 250 ml of
 anhydrous ether containing 1 mole % of Ni(II)DPPPCl₂-
 catalyst. The reaction mixture was turned overnight and
 hydrolyzed on the next morning with 100 ml of HCl 5 % in
 water. The aqueous phase was neutralize and the product
 20 was extracted with several portions of ether, which was
 finally evaporated. The product (3), 6-(p-styryl)-
 bromohexane was purified by column-chromatography using
 hexane as solvent. 20.2 g of 1-bromo-6(p-styryl)-hexane =
 76 % of the theoretical yield were isolated.

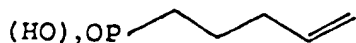
6-(p-styryl)hexyl-trimethoxysilane compound (5)

0.05 mole (13.3 g) of compound (3) were added to 1.3 g
 magnesium turnings in ether as described above. The
 obtained Grignard compound was dropped in a THF-solution of
 30 0.05 mole (7.9 g) chloro-trimethoxysilane cooling to -60°C.
 The solution was allowed to warm up to room temperature and
 stirred for 15 hours before being filtered. The THF was
 pumped of and the residue mixture was extracted with
 pentane. The solvent was evaporated and the product
 35 distilled under vacuum (B.p. = 142°C at ~0.1 mm Hg) to

afford 10.9 g (70 %) 6-(p-styryl) hexyl-trimethoxysilane.

EXAMPLE 3: Preparation method for 4-pentene-phosphonic acid

5 4-pentene-phosphonic acid



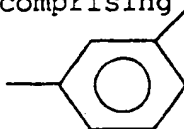
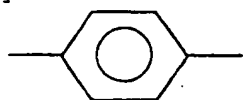
10 Reaction step:



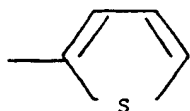
Phosphonic acids (often called phosphonates) were prepared
 15 by Michaelis-Arbuzov reaction of the corresponding
 haloalkanes with triethyl-phosphite, 0.02 mole (2.98 g) of
 5-bromo-1-pentene and 0.0 mole (8.3 g) triethyl-phosphite
 were refluxed 150° for 65 hours. The solution was cooled
 to room temperature and hydrolysed with 30 ml of
 20 concentrated aqueous HCl. Heating was resumed for another
 16 hours. After cooling, 10 ml of water were added and the
 aqueous phase separated and the water evaporated on air
 during 2 days. The precipitated product was washed with
 p.A. acetonitrile and dried under vacuum.

25 By selecting a specific bifunctional coupling
 agent, it is possible to control, to some extent, the
 strength of the adhesion of the bifunctional coupling agent
 to the metal surface. For example, when constituent part X
 is an alkoxy silane and R^S is a chain comprising

30



and/or



units, the presence of

35

electron withdrawing or electron donating substituents on said units will influence the strength of the adhesion of the monolayer to the metal surface.

The present invention also concerns a method of
5 treating a metal surface with the bifunctional coupling agent $X-R^S-Y$. Said method comprises the step of applying a monolayer of $X-R^S-Y$ onto a metal surface.

This can be performed in a multitude of manners.

The metal surface can be coated with primer
10 composition which is a suitable solution of $X-R^S-Y$. This can be effected by dipping, spraying, electrochemical deposition or other known coating techniques.

The monolayer can also be formed by vapour deposition of $X-R^S-Y$ on the metal surface.

15 An alternative method is plasma deposition.

The presence of a monolayer of $X-R^S-Y$ on the metal surface and the homogeneous quality of same can be verified by HREELS "High Resolution Electron Energy Loss Spectroscopy".

20 According to the present invention, it is preferred that the metal surface should be covered with a closely packed monolayer and not more than a monolayer.

Excess $X-R^S-Y$ present on the metal surface should be removed before applying the non-metallic coating onto
25 the metal surface or before incorporating the metal element into the non-metallic medium e.g. for reasons of reinforcement. Removal of excess $X-R^S-Y$ can be performed by known techniques, such as by vacuum treatment, by rinsing the metal surface with a suitable solvent followed by
30 drying, or by ultrasonic rinsing.

Side-products may be produced during deposition of the $X-R^S-Y$ monolayer on the metal surface. This is for example the case when constituent part X is a alkoxysilane

group. ROH, whereby -OR is an alkoxy group of the alkoxy silane, is then produced as a side-product of the surface chemisorption reaction. As such side-products are liable to disturb the regular structure of the monolayer, they must as much as possible, be eliminated from the metal surface and the monolayer.

Thereto, the same methods can be used as for removing surplus $X-R^S-Y$.

If the monolayer was applied by means of a solution of $X-R^S-Y$, whereby the solvent is not compatible with the non-metallic medium, residues of the solvent in or on the monolayer should also be removed.

As mentioned above, bifunctional coupling agents of the present invention present the important tendency of forming Self-Assembled Monolayers on the metal surface.

Despite the tendency of the $X-R^S-Y$ bifunctional coupling agent to form a Self-Assembled Monolayer, some anomalies may be present. These anomalies are preferably eliminated from the monolayer by means of a thermal tempering treatment, at a temperature depending on the chemical nature of the constituent part X group (e.g. when X is a silane group, tempering may be conducted at $\sim 200^\circ\text{C}$; when X is a thiol group tempering may be conducted at $\sim 100^\circ\text{C}$).

Prior to depositing the $X-R^S-Y$ monolayer, it will generally be necessary to subject the metal surface to a cleaning treatment so as to remove therefrom scale and other contaminants or substances likely to hinder the adhesion of the $X-R^S-Y$ bifunctional coupling agent to the metal surface via its constituent part X.

Such cleaning can be effected by a known thermal, mechanical or chemical cleaning process or a combination of such processes, which could for instance be

a descaling process.

According to the present invention, it has been found that, that molecules of the above-defined formula $X-R^S-Y$ allow to realize a strong and lasting adhesion between, on the one hand, a range of metal surfaces and, on the other hand, a range of non-metallic media, by means of a purposeful selection of all three of the constituent parts X, R^S and Y .

In order to obtain good adhesion, the concentration of the constituent parts Y on the surface of the monolayer not attached to the metal surface must be high.

This is achieved by a purposeful choice of constituent part R^S , which must permit and preferably promote a close packing of the monolayer.

An additional important advantage of the present invention is that it effectively inhibits corrosion of the metal surface through the presence of the constituent parts X on the metal surface and through the close packing of the layer.

The said corrosion inhibiting effect is further enhanced when constituent part R^S is fluorinated.

An additional advantageous consequence of this corrosion-inhibiting effect of the monolayer according to the invention is that metal elements, the metal surface of which has been covered with said monolayer, may be stored for a longer period of time before being processed further.

As stated above, when constituent part R^S is $-(CH_2)_n-$ n may vary between 2 and 20, preferably between 4 and 20.

A value of $n < 10$ allows for an electrochemical activation from the metal, via X and R^S , to constituent part Y for the coupling of Y to the non-metallic medium.

A high value of n (>12) provides for better corrosion inhibition by passivation and blocking of the metal surface.

Halogenation -preferably fluorination- of said -
5 $(CH_2)_n$ - chains not only increases corrosion inhibition due to increased hydrophobicity, it also confers lubrication properties on the monolayer. In many applications this is a significant advantage for the further processing of the metal element.

10 For a better understanding of embodiments of the invention below an exemplary method of coating steel cords with a composition of the invention and preparation of such a composition is given :

15 Preparation:

Step 1 : Hydrolysis of an amount of 3-Amino-propyl-trimethoxysilane (APTS) (I). Example for
20 preparing 1-2 litres of poly-condensed silane (polysiloxane) solution, ready for use. 300-900 μ l (1-3 eq in relation to OR functions) of water are added to 1 ml of compound (I) under stirring, the hydrolysis starts instantaneously. The temperature during the polycondensation might
25 be increased to 65-70°C, in order to obtain a higher degree of condensation. After the hydrolysis supplementary water can be added (1-3 vol %) to avoid precipitation of the silane or polysiloxane. Short ageing (5-10 minutes) of
30 the solution may contribute to the chain length and by this to the interfacial interaction between the metal surface and rubber.

Step 2 : Hydrolysis of the surface active silane [6-(p-styryl)hexyltrimethoxysilane]. The
35 solution obtained from step 1 is diluted with 9

ml of methanol and 1 ml of water. 9 ml of the surface active coupling agent II are added under stirring at 60°C. The solution is ready for use after 5 minutes. This solution is further diluted to 1 l with methanol to yield a final solution of 1 % of II.

Cord coating :

10 Zinc coated steel cords are dipped for 1 second in the above solution and dried for 10 minutes at 65°C. The coated steel cords are subsequently embedded in a natural rubber compound. The composite is put in a rubber curing press for 20 minutes at a temperature of 150°C.

15

Below some experimental results are given concerning adhesion to and corrosion of different substrates.

EXPERIMENTAL RESULTS

20

I. Adhesion in natural rubber, polyurethane and thermoplastic rubber.

A. Preparation of samples.

25

All samples start from a 7x0.35 zinc coated steel cord.

Sample n° 1 : type of preparation : direct chromatation

30 Step 1 : A zinc coated steel cord is rinsed with demineralised water. The sample is subsequently dipped for two seconds in a 0.5 % HNO₃ solution. The sample is rinsed again with demineralised water and further dipped in a 1.5 % Corrolyellow® solution (marketed by Atochem) for 35 45 seconds. The sample is rinsed twice with

demi water and finally dried with ethanol and ether.

Step 2 : The sample prepared as in step 1, is now dipped for twenty seconds in a solution of an anorganic silicate : Corosil® 401 (150 ml/l) + Corrosil® 407 (5 ml/l) at a pH of 10.05 ± 0.05 . The sample is subsequently dried at 70°C during ten minutes.

The previous steps are done to supply the surface with chromates. Corrolyellow comprises chromium in the form of chromates. Such provision of chromates constitutes a preferred pretreatment of the surface.

Step 3 : The sample as prepared in step 2, is now dipped for 60 seconds in a 3 % primer solution of 3-trimethoxysilylpropyl diethylenetriamine in absolute ethanol containing 5 ml of NaOH (final pH : 8.49). The sample is further dried in the air for five minutes and finally dried during ten minutes at 60°C.

Sample n° 2 : type of preparation : electrochemical molybdenisation

Step 1 : A sample is dipped during 2 seconds in a solution (100 g/l) of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ under a 3 V AC source at 40°C. The counter electrode is a plate of stainless steel. The sample is subsequently rinsed with demi water and dried with ethanol and ether. Hereby Molybdenum is supplied to the surface of the steel cord.

Steps 2 and 3 : same as for sample n° 1.

Sample n° 3 : type of preparation : Electrochromatation.

Step 1 : A sample is dipped during three seconds in an electrochemical cell at 50°C containing the

following electrolyte (50 g/l) : $K_2Cr_2O_7$; 30
g/l $ZnSO_4$ and 20 ml/l acetic acid. Current
density is about 70 A/dm². Voltage is 2.5 V.
The counter electrode is a platina electrode.
The sample is subsequently rinsed with demi
water and dried in ethanol and ether. This pre-
treatment provides for chromium on the steel
cord.

Steps 2 and 3 : same as for sample n° 1.

Sample n° 4 : type of preparation : direct chromatation.

Step 1 : same as for sample n° 1

Step 2 : The sample as prepared in step 1 is dipped
during twenty seconds in a solution of
bistriethoxysilyl ethane (BTSE) (4% BTSE + 20%
water in absolute ethanol ; pH : 5.5-6.5)
The sample is dried in the air during three
minutes and finally dried at 70°C during ten
minutes.

Step 3 : same as for sample n° 1

Sample n° 5 : type of preparation : electrochemical
molybdenisation.

Step 1 : same as for sample n° 2

Step 2 : same as for sample n° 4

Step 3 : same as for sample n° 1

Sample n° 6 : type of preparation : electrochemical
chromatation.

Step 1 : same as for sample n° 3

Step 2 : same as for sample n° 4

Step 3 : same as for sample n° 1

Sample n° 7

Step 1 : same as for sample n° 1

Step 2 : same as for sample n° 2

Step 3 : The sample as prepared in step 2, is dipped during 60 seconds in a 3 % primer solution of 3-mercaptopropyl triethoxysilane (MPTS) in absolute ethanol containing 5 ml NaOH (final pH : 8.49). The sample is further dried in the air during five minutes and finally dried during 10 minutes at 60°C.

10 Sample no 8

Step 1 : same as for sample n° 1

Step 2 : is omitted

Step 3 : same as for sample n° 7

15 Sample n° 9 and 10

3-amino-propyl-trimethoxysilane (APTS) is used as a bifunctional coupling agent and is hereafter referred to as silane.

20

A prereaction or hydrolysis of silanes is preferably done, prior to the use of the solution. This is done on the pure silane before dilution. The following steps are followed to hydrolyse the silane :

25

1. An amount of silane is poured in a beaker or measuring cylinder. Slowly add an amount of water equal to 2 equivalents compared to the number of silane groups present on the molecule. 2 Si-groups equals 4 equivalents of water added, 3 Si-groups equals 6 equivalents of water added to the silane.

30

2. While the water is added, stir thoroughly. If hydrolysis takes place, the silane and the water will mix and produce heat. After a while, a reflux effect at the surface of the liquid will be seen, indicating

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that the alcohol is formed out of the water and the silane. The alcohol evaporates and recondenses at the colder glass surface.

3. After some time after all the water is added, the liquid will show a higher viscosity compared to the original mixture. This is also an indication that hydrolysis has taken place.
4. The liquid is now ready to use. Further usage may be dilution in alcohol, water or another solvent (mixture) in order to reach a certain concentration to be used in an application. Further usage can also be addition to another prereacted silane, etc.
5. A 40 % solution of sodium silicate with 5 % of silane is made by mixing 400 ml of silicate with 200 ml of water. Hydrolysed silane, as prepared hereabove, is added to an end concentration of 5 % silane. Adjust with water to reach 1000 ml. The end concentration of the primer solution is then 40 % Na_2SiO_3 with 5 % silane. The primer solution can be used pure or diluted 1/2 with water.

Sample n° 11 :

Starting silane is triethoxysilyl poly-1,2 butadiene. This silane is dissolved under reflux in heptane/toluene 10:1. The wire is dipped in a boiling solution, dried during one hour in air followed by a drying step of 15 minutes at 110 °C.

B. Adhesion to polyurethane (marketed by Bayer under Desmopan® 322/7)

The adhesion strength is quantified by the pull out force as per ASTM D2229. A specified length of a steel element (cord or wire) is embedded in polyurethane and the force necessary to pull the elements linearly out of the

polyurethane is measured. The embedded length of the sample is 25 mm. The pull out speed is 100 mm/min and the circle of the pull out clamp is 12.7 mm. Prior art stands for untreated zinc coated steel cord.

5

Sample number	Pull out force (Newton)
Prior art	405 374
1	843
2	573
3	772
4	678
5	528
6	577
9	885
10	759

C. Adhesion to natural rubber.

10 The composition of the rubber is : natural rubber : 100 parts, carbon black N300 : 60 parts per hundred rubber (phr), oil : 11 phr, zinc oxide : 5 phr, stearic acid : 1 phr, 6-ppd : 1 phr, sulphur : 2.5 phr, MBS : 0.6 phr.

15

Adhesion is quantified by the pull out force as per ASTM D2229. The embedded length is 25 mm. The vulcanisation temperature was 150°C and vulcanisation time was 20 minutes. The pull out speed is 100 mm/min, and the
20 circle of the pull out clamp is 12.7 mm. Prior art stands for untreated zinc coated steel cord.

Sample number	Pull out force (Newton)
Prior art	71 73
7	275
8	241
11	453

C. Adhesion to thermoplastic rubbers (Santoprene®
5 marketed by AES)

The embedded length is here 40 mm. The pull out speed is
50 mm/min. Prior art stands for untreated zinc coated
steel cord.

10

Sample number	Pull out force (Newton)	Pull out force (Newton)
	Santoprene 101-84	Santoprene 191-85A
Prior art	131	240
1	410	402
3	367	263

D. Adhesion to a conventional hose rubber compound.

15

Sample number	Pull out force (Newton)
Prior art	73
11	922

E. Adhesion in concrete.

Preparation of samples.

5

The prereaction or hydrolysis of silanes is preferably done, prior to the use of the primer solution. This is done on the pure silane before dilution. The steps given in samples 9 and 10 above are followed to hydrolyze the
10 silane.

Sample n° 12 :

Step 1 : Hydrolysis of a effective amount of 3-amino-propyl-trimethoxysilane (APTS).

15 Step 2 A 40 % solution of sodium silicate with 5 % of silane is made by mixing 400 ml of silicate with 200 ml of water. Hydrolysed silane, as prepared in step 1, is added to an end concentration of 5 % silane. Adjust with water to reach 1000 ml.
20 The end concentration of the solution is then 40 % Na_2SiO_3 with 5 % silane. The primer solution can be used pure or diluted 1/2 with water.

25 Sample n° 13

Same as sample n° 12 but with 3-mercapto-propyl-trimethoxysilane (MPTS) instead of 3-amino-propyl-trimethoxysilane (APTS).

30 Test results.

The adhesion strength is measured as the pull out force of a straight wire out of concrete.

	Sample	Pull out force (Newton)
No furnace	Prior art wire+brass coating	56.4
No furnace	Wire+brass+ 0.50 % coating as prepared under sample no 12	33.1
No furnace	Wire+brass+ 2.50 % coating as prepared under sample no 12	80.2
Furnace	Prior art Wire+brass	26.3
Furnace	Wire+brass+ 2.50 % coating as prepared under sample no 12	97.0

In the table hereabove, the ends of the wire are always out of the concrete. In the table hereunder one end of the wire is in the concrete.

5

	Sample	Force (Newton)
No furnace	Prior art Wire+brass coating	296.8
No furnace	Wire+brass+ 10 % coating as prepared under sample no 13	344.8

II. Corrosion behaviour.

10 A. Corrosion test.

The corrosion behaviour of the steel cords and steel

wires covered with the coatings according to the invention have been performed in accordance with ASTM MNL20(1995), pp. 76-80 and ASTM test specification G5-87.

5 Some requirements in the ASTM G5-87 specification could not be attained due to the nature of the specimens. With respect to section 4.7.1. of ASTM G5-87, instead of a rod a steel cord, bead wire or steel wire was used as a sample. The sample was mounted in a teflon sampleholder
10 according to Figure 1. Figure 1 substitutes ASTM G5-87- Fig 3. Furthermore, 5 cm of the cord was exposed to the corrosive liquid, the remaining cord was coated with a lacquer. Section 4.7.2. : high density graphite counter electrodes were used instead of platinum electrodes, this
15 in accordance with section 4.7.2.3. With respect to Section 5.1., the electrolyte 0.1 N sulphuric acid is substituted with 0.05 molar potassium sulphate. With respect to section 5.111.1, the polarisation scan is carried out after 1000 seconds instead of after 1 hour of
20 immersion.

From the data, the polarisation resistance R_p and the corrosion current density I_{corr} is calculated in accordance with ASTM G3-89 and ASTM G102-89. The higher the
25 polarisation resistance, the longer the corrosion resistance of the tested steel cord. The higher the corrosion current density, the higher the degree of corrosion. In order to have a rating of the corrosion resistance, the so called "inhibiting rating" is
30 calculated as defined in "Compendium of Chemical Terminology", IUPAC Recommendations, Blackwell Scientific Publications, 1987, p 198 :

$$I = (V_o - V) / V_o$$

With I the corrosion inhibition rating
(in percent)

V_o the corrosion rate of non treated steel cord or
steel wire ; $V = 1 / R_p$

5 V the corrosion rate of treated steel cord or
steel wire ; $V_o = 1 / R_p$

First corrosion test

10 Samples for first corrosion test.

Prior art sample 14 : galvanized wire for bead
reinforcement.

Sample n° 15 : galvanized wire for bead reinforcement
15 treated with 1/3 concentration of 3-aminopropyltri-
etoxy silane.

Prior art sample 16 : galvanized steel cord.

Sample n° 17 : galvanized steel cord treated with 1/3
20 concentration of 3-aminopropyltriethoxy silane.

Sample n° 18 : galvanized steel cord treated with ≤ 0.5 %
of trimethoxysilylpolyethylene.

25 Results of first corrosion test.

Sample	R_p (kohm)	I_{corr} ($\mu A/cm^2$)	I (%)
Prior art no 14	2.64	3.39	-2.27
	2.84	3.15	5.08
	2.94	3.04	8.18
	2.37	3.77	-13.69
Sample no 15	22.63	0.40	88.08
	250.	0.04	98.92
	8.12	1.10	66.81

	48.89	0.18	94.48
--	-------	------	-------

Sample	R_p (kohm)	I_{corr} ($\mu A/cm^2$)	I (%)
Prior art no 16	4.68	12.23	
Sample no 17	39.06	0.56	88.03
Sample no 18	16.47	1.32	71.59

5

Second corrosion test

Samples for second corrosion test : corrosion potential in high-performance concrete.

10 Prior art : zinc plated steel cord.

Sample n° 19 : zinc plated steel cord treated with 0.01 % solution of 3-aminopropyltriethoxysilane (APTS).

Sample n° 20 : zinc plated steel cord treated with 0.1 % solution of 3-aminopropyltriethoxysilane (APTS).

15 Sample n° 21 : zinc plated steel cord treated with 1 % solution of 3-aminopropyltriethoxysilane (APTS).

Sample n° 22 : zinc plated steel cord treated with 1 % solution of (3-methoxysilylpropyl)diethylenetriamine.

20

Results of second corrosion test : corrosion potential in high-performance concrete.

25

30

Corrosion potential (mV versus saturated calomel)

Sample	After 5 sec	After 10 sec	After 100 sec	After 500 sec	After 1000 sec
Prior	-1319	-1317	-1322	-1007	-895
art	-1357	-1356	-1349	-1292	-915
	-1345	-1343	-1341	-1289	-1008
No 19	-874	-870	-850	-915	-1010
No 20	-836	-825	-782	-746	-771
No 21	-819	-815	-796	-913	-1172
No 22	-862	-859	-796	-759	-759

The corrosion potential is the potential of a corroding surface in an electrolyte relative to a reference electrode measured under open circuit conditions (source : ASTM G15-93).

The value below which hydrogen may be formed lies somewhere between -1000 mV and -1100 mV. As may be derived from the table, hydrogen can be formed with all prior art samples. With respect to the samples treated according to the invention, only with sample n° 3 hydrogen may be formed.

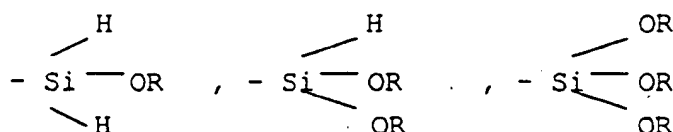
The above given experimental results show that the invention provides substantial advantages over the prior art.

C L A I M S

1.- Primer composition for improving the surface
 5 adhesion between a metal surface and a non-metallic medium,
 characterized in that it comprises a bifunctional coupling
 agent of the formula $X-R^S-Y$, whereby constituent part X is a
 functional group selected among :

x.a)

10



mono-, di- and tri-chlorosilane groups and mono-, di- and
 tri-bromosilane groups, whereby each -OR is the same and is
 15 a methoxy or an ethoxy group,

x.b) $-\text{CO}_2\text{H}$, $-\text{PO}_3\text{H}_2$ and $-\text{SO}_2\text{H}$, their acid anhydride and
 their acid chloride groups,

x.c) an organometallic group of the formula $-\text{M}(\text{OR})_n$ or
 $-\text{M}(\text{Cl})_n$, whereby M is a metal selected from the group
 20 comprising Al, Sn, B, Ti and V, and whereby each -OR is the
 same and is a methoxy or an ethoxy group, n being the
 ligand number corresponding to the metal M,

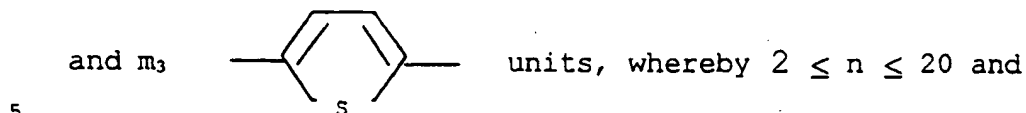
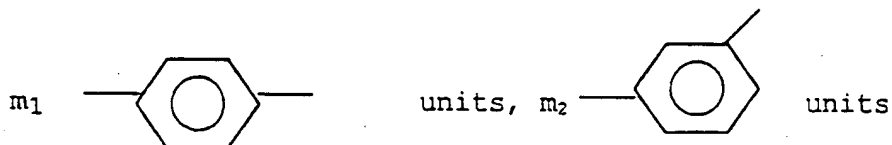
x.d) a phthalocyanin or a phthalonitril group,

x.e) a monothiol or a monothiolate group,

25 whereby constituent part R^S is selected among :

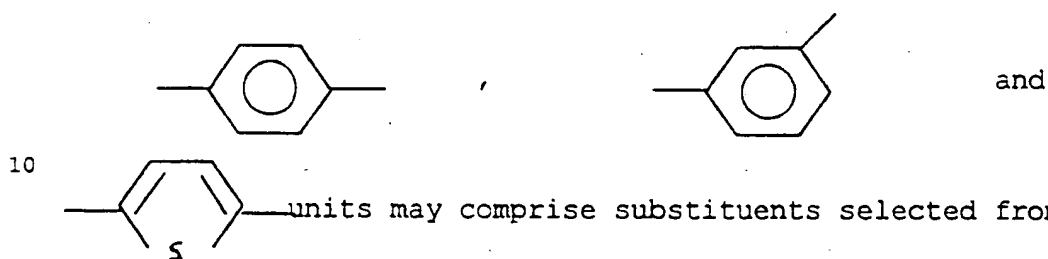
rs.a) a $-(\text{CH}_2)_n-$ chain, whereby $2 \leq n \leq 20$ and whereby
 said chain may be unhalogenated, partially halogenated or
 perhalogenated,

rs.b) a chain consisting of n unhalogenated, partially
 30 halogenated or perhalogenated $-(\text{CH}_2)-$ units,




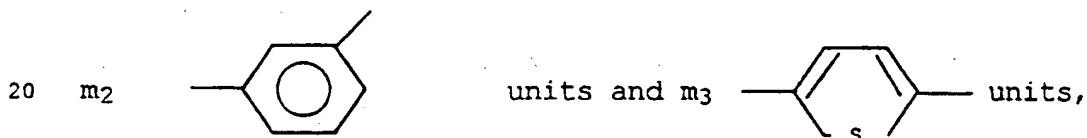
5

$0 < (m_1 + m_2 + m_3) \leq 3$ and whereby some or all of the



the group comprising: $-(CH_2)_iCH_3$ with $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$ with $0 \leq j \leq 4$, $-O(CF_2)_jCH_3$ with $0 \leq j \leq 4$, $-C \equiv N$ and $-NH_2$,
 15 rs.c) an unhalogenated, partially halogenated or

perhalogenated chain consisting of m_1  units,



whereby $2 < m_1 + m_2 + m_3 < 6$, and whereby said units may comprise substituents selected from the group comprising :
 $-(CH_2)_iCH_3$ with $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$ with $0 \leq j \leq 4$,

25 $-O(CF_2)_jCH_3$ with $0 \leq j \leq 4$, $-C \equiv N$ and $-NH_2$,

and whereby constituent part Y is a functional group selected among :

y.a) an unsaturated terminal double or triple carbon-carbon bond,

30 y.b) an acrylic or methacrylic acid group and its methyl or ethyl esters,

y.c) $-NH_2$ or $-NHR$, whereby R is a methyl or ethyl

group,

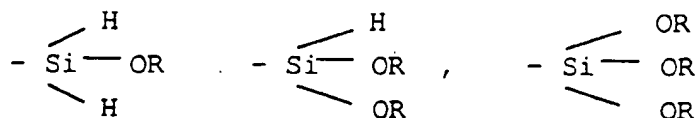
y.d) $-C\equiv N$,

y.e) an activated carboxylic ester,

y.f) an aldehyde group,

5 y.g) an epoxide group,

y.h)

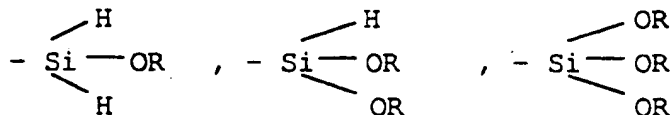


10 a mono-, di- and tri-chlorosilane group and a mono-, di- and tri-bromosilane group, whereby each -OR is the same and is a methoxy or an ethoxy group, provided R^S is an unhalogenated, partially halogenated or perhalogenated $-(CH_2)_3-$ or $-(CH_2)_4-$ chain,

15 y.i) a functional group capable of forming a complex with at least one ingredient of the non-metallic medium.

2. Primer composition for improving the surface adhesion between a metal surface and a non-metallic medium, characterized in that it comprises a bifunctional coupling agent of the formula $X-R^S-Y$, whereby constituent part X is a functional group selected among :

x.a)



25

mono-, di- and tri-chlorosilane groups and mono-, di- and tri-bromosilane groups, whereby each -OR is the same and is a methoxy or an ethoxy group,

x.b) $-CO_2H$, $-PO_3H_2$ and $-SO_2H$, their acid anhydride and their acid chloride groups,

30

x.c) an organometallic group of the formula $-M(OR)_n$ or $-M(Cl)_n$, whereby M is a metal selected from the group comprising Al, Sn, B, Ti and V, and whereby each -OR is the same and is a methoxy or an ethoxy group, n being the

ligand number corresponding to the metal M,

x.d) a phthalocyanin or a phthalonitril group,

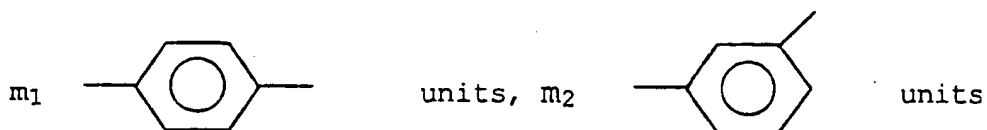
x.e) a monothiol or a monothiolate group,

whereby constituent part R^S is selected among :

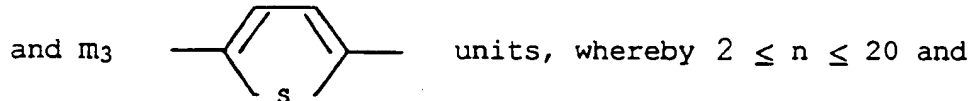
5 rs.a) a $-(CH_2)_n-$ chain, whereby $2 \leq n \leq 20$ and whereby said chain may be unhalogenated, partially halogenated or perhalogenated,

rs.b) a chain consisting of n unhalogenated, partially halogenated or perhalogenated $-(CH_2)-$ units,

10

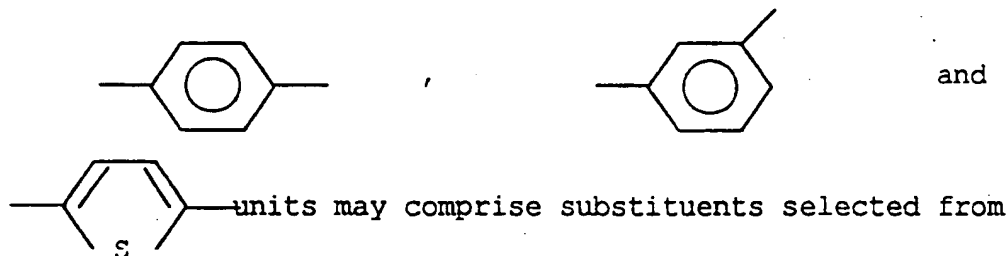


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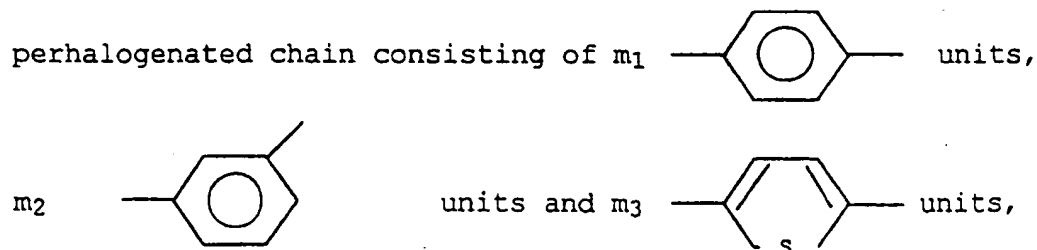
$0 < (m_1 + m_2 + m_3) \leq 3$ and whereby some or all of the

20



25 the group comprising: $-(CH_2)_iCH_3$ with $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$ with $0 \leq j \leq 4$, $-O(CF_2)_jCH_3$ with $0 \leq j \leq 4$, $-C \equiv N$ and $-NH_2$,
rs.c) an unhalogenated, partially halogenated or

30



whereby $2 < m_1 + m_2 + m_3 < 6$, and whereby said units may comprise substituents selected from the group comprising :

$-(CH_2)_iCH_3$ with $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$ with $0 \leq j \leq 4$,

$-O(CF_2)_jCH_3$ with $0 \leq j \leq 4$, $-C \equiv N$ and $-NH_2$,

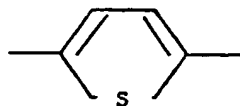
5 and whereby constituent part Y is $-Si-OH$ or $-Si-ONa$.

3. Primer composition for improving the surface adhesion between a metal surface and a non-metallic medium, characterized in that it comprises a bifunctional coupling agent of the formula $X-R^S-Y$, whereby constituent part X is a
10 alkoxysilane and R^S is a chain comprising



15

or



units, and whereby constituent

part Y is a functional group selected among :

20 y.a) an unsaturated terminal double or triple carbon-carbon bond,

y.b) an acrylic or methacrylic acid group and its methyl or ethyl esters,

25 y.c) $-NH_2$ or $-NHR$, whereby R is a methyl or ethyl group,

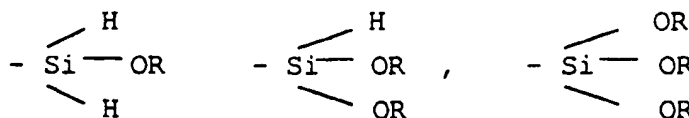
y.d) $-C \equiv N$,

y.e) an activated carboxylic ester,

y.f) an aldehyde group,

y.g) an epoxide group,

30 y.h)



a mono-, di- and tri-chlorosilane group and a mono-, di-

and tri-bromosilane group, whereby each -OR is the same and is a methoxy or an ethoxy group, provided R^S is an unhalogenated, partially halogenated or perhalogenated $-(CH_2)_3-$ or $-(CH_2)_4-$ chain,

- 5 y.i) a functional group capable of forming a complex with at least one ingredient of the non-metallic medium.

4.- Primer composition according to claim 1, 2,
10 or 3, characterized in that X is a monothiolate group selected from the group comprising -SNa and -SK.

5.- Primer composition according to any one of claims 1 to 4, characterized in that R^S is a partially fluorinated or perfluorinated $-(CH_2)_n-$ chain.

15 6.- Primer composition according to any one of claims 1 to 5, characterized in that Y is a terminal double carbon-carbon bond and R^S is such that $-R^S-Y$ terminates in any one of the following groups: vinyl, allyl, styryl, thienylvinylene, phenyl, pyrrole.

20 7.- Metal element, characterized in that at least part of the metal surface of said element is covered with an layer obtained by reaction of a bifunctional coupling agent of the formula $X-R^S-Y$ on the metal surface, whereby $X-R^S-Y$ is as defined in any one of claims 1 to 6.

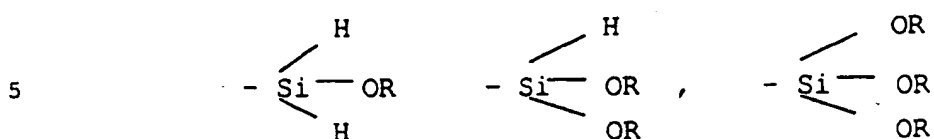
25 8.- Element according to claim 7, characterized in that the metal surface is mainly made of Al, Fe, Ni, Cu, Zn, Ag or alloys of these metals.

9.- Element according to claim 8, characterized in that the element is a basic metal element coated with a
30 metal coating of a brass, bronze, zinc or zinc alloy.

10.- Element according to claim 9, characterized in that the basic metal element consists essentially of steel.

11.- Element according to any one of claims 7 to

10, characterized in that the metal surface is mainly made of Zn, whereby the constituent part X is selected among



whereby each -OR is the same and is a methoxy or an ethoxy group,

mono-, di- and tri-chlorosilane groups and mono-, di- and tri-bromosilane groups,

- CO₂H, -PO₃H₂ and -SO₂H, and their acid anhydride and their acid chloride group,

- a monothiol and a monothiolate group, and

- a phthalocyanin and a phthalonitril group

12.- Element according to any one of claims 7 to 10, characterized in that the metal surface is mainly made of a Zn-Cu alloy, whereby the constituent part X is selected among the group comprising :

- a phthalocyanin and a phthalonitril group,



whereby each -OR is the same and is a methoxy or an ethoxy group

and mono-, di- and tri-chlorosilane groups, and mono-, di- and tri-bromosilane groups,

13.- Element according to any one of claims 7 to 10, characterized in that the metal surface is mainly made of a steel, whereby the constituent part X is selected among

- a monothiol and a monothiolate group,

- a phthalocyanin and a phthalonitril group.

14.- Element according to any one of claims 7 to 13, characterized in that constituent part Y is a double carbon-carbon double or triple bond and whereby the part of

the metal surface which is covered with the monolayer is further covered with a polyethylene, polypropylene, polybutadiene, a copolymer of at least two of ethylene, propylene and butadiene, or a rubber coating.

5 15.- Use of a metal element according to any one of claims 7 to 12 for the reinforcement of polyurethane, polyethylene, polypropylene, polybutadiene, a copolymer of at least two of ethylene, propylene and butadiene, rubber, polyacrylate, polyamide or concrete, in particular high
10 performance concrete and whereby the metal element is elongated in shape.

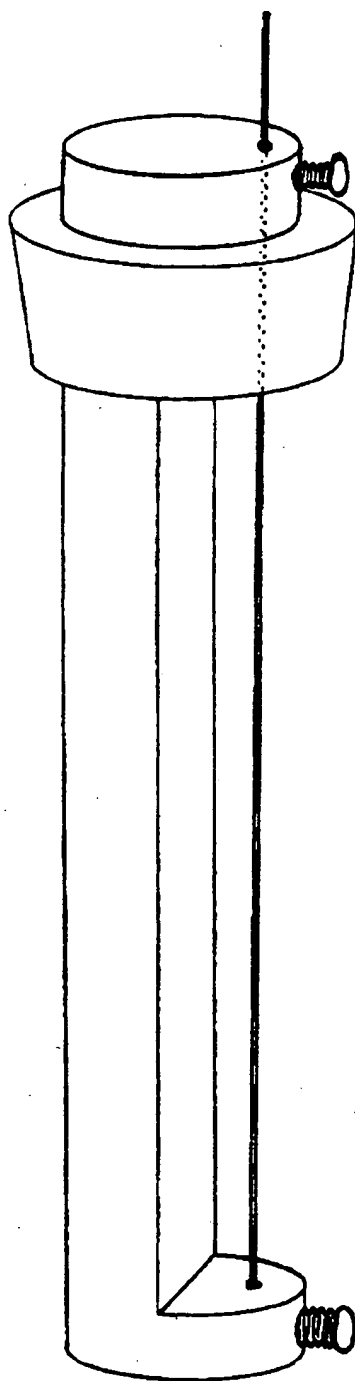
 16. Method of manufacturing an object comprising a metal element and a non-metallic medium said method comprising the step of providing the metal element with a
15 layer of a bifunctional coupling agent of the formula $X-R^S-Y$ on the metal surface, whereby functional group X enables a strong adhesion of the coupling agent to the metal surface, functional group Y provides for strong adhesion to the non-metallic medium and R^S acts as a spacing agent between
20 function X and Y and adhering the metal element and the non-metallic medium to each other.

 17. Method of manufacturing as claimed in claim 16, characterized in that $X-R^S-Y$ is as defined in any one of
25 claims 1 to 6.

 18. Method of manufacturing an object as claimed in claim 16 or 17, characterized in that the metal is prior to providing the layer provided with a chromium or molybdenum containing pre-layer.

30 19. Method as claimed in claim 18, characterized in that the pre-layer comprises chromate.

I/I



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/BE 98/00153

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP 0 802 217 A (CONTINENTAL AG) 22 October 1997 see claims 1-11 see page 2, line 49 - line 52 ---	1,5,13
A	EP 0 331 279 A (ICI PLC) 6 September 1989 see claims 1-12 ---	1
A	US 5 126 385 A (SEIBERT REBECCA F ET AL) 30 June 1992 see claim 1 ---	1
A	EP 0 738 748 A (MICHELIN & CIE) 23 October 1996 cited in the application see claims 1,11 ---	1
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Z document member of the same patent family

Date of the actual completion of the international search

2 February 1999

Date of mailing of the international search report

11/02/1999

Name and mailing address of the ISA

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Authorized officer

Depijper, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 98/00153

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 383 150 A (MICHELIN & CIE), 22 August 1990 see claims 1-21 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE 98/00153

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